Field-induced strain associated with polarization reversal in a rhombohedral ferroelectric ceramic

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The polarization reversal process in a rhombohedral ferroelectric ceramic material was investigated using field-induced strain measurements and texture development. Special attention was focused on the difference in the field-induced strains between the first quarter cycle and subsequent loading conditions. Results show that the initial field-induced strain is about twelve times greater than the subsequent strain, which immediately suggests that mechanisms involved in these conditions during the polarization reversal process are different. The difference in the magnitude of field-induced strain is discussed in terms of 180° and non-180° domain reorientation processes.

I. INTRODUCTION

Ferroelectic ceramics have found many technical applications due to the development of spontaneous polarization during the paraelectric (PE)-to-ferroelectric (FE) phase transformation. For most applications, the materials are made either of polycrystalline ceramics or thin layers that need to be electrically poled to be piezoelectrically active. It is well known that the poling process involves (i) a domain reorientation process to maximize the resolved dipole moment in the crystalline lattice to the applied field direction, (ii) a converse piezoelectric effect by stretching the dielectric dipole by the electric field, and (iii) a higher order nonlinear electrostrictive effect under extremely high field conditions. Because the third process is not pertinent to the subject, it will not be discussed in this study.

When the material breaks the symmetry from a high temperature cubic PE phase to a low symmetry FE phase a spontaneous strain develops along the polarization direction. During the poling process, as the dipoles are reoriented, the material will be subjected to a deformation in which the field-induced strain parallel to the electric field direction increases [as illustrated by the longitudinal (//) strain loop at 75 °C in Fig. 1], while transverse to the field direction the strain decreases [compare to the transverse (⊥) strain loops at 25 or 105 °C in Fig. 1]. As a result of this deformation, a large stored elastic strain energy is developed in the partially electroded ceramic components, which makes these components more prone to cracking.[1,2] Data presented in Fig. 1 were collected when the material was first subjected to an electric field (sometimes these curves are called "virgin curves"). Notice the magnitude of the initial field-induced strain in the first quarter cycle, which is much greater than that of the rest of the cycle. The connection between this large initial

field-induced strain and cracking in electroceramic components was reported recently.[3] The fundamental mechanism with respect to the field-induced strain between the initial and the subsequent polarization reversal is not fully understood and is a subject of this investigation. In this paper, we will review some important aspects of this process and present some new observations in a tin modified lead zirconate titanate ceramic [$Pb_{0.99}(Sn_{0.13}Zr_{0.82}Ti_{0.05})_{0.98}Nb_{0.02}O_3$ (PSZT)].

It is well known that polarization reversal in ferroelectrics is a nucleation and growth process[4,5] in which the coercive field (E_c, or the threshold field for reversing the polarization direction) is strongly dependant on the kinetic conditions such as the electrical driving frequency or pulsing field strength.[6,7] Therefore, the term "polarization reversal" or "domain reorientation" used in the paper refers to a nucleation and growth process. Based on the optical observation and dynamic measurements of barium titanate single crystals,[4,6] when the applied electric field is reversed new domains with a wedge shape will nucleate and grow quickly in an old domain in the forward direction. However, in some cases even if a high reverse field is applied, small regions with opposite polarization cannot be completely removed in a single crystal.[6] It has also been observed that the domain nucleation and growth process is extremely sensitive to the elastic clamping on the crystal.[6] These features could be important when one tries to understand the polarization reversal process in polycrystalline ceramics.

II. EXPERIMENTAL

The tin modified lead zirconate titanate ceramic (PSZT) used in this investigation possesses a rhombohedral pervoskite structure in which the spontaneous polarization can be developed in eight equivalent directions

[111] and form 71° (or 109°) and 180° domains during the PE-to-FE phase transformation. Samples were prepared by a conventional mixed oxide method (Alliant Corporation, Minneapolis, MN). Test samples were sliced and ground from the sintered ceramic, and were subsequently electroded with a fired on silver paste (DuPont 7095, Wilmington, DE). The electrically induced strains developed parallel (//) to the poling direction and perpendicular (⊥) to the poling direction were determined by a linear variable differential transformer and strain gauge technique,[8] respectively.

The field-induced strains reported in Figs. 1 and 2 were measured from samples with a thin disk geometry (5.0 mm diameter, 0.25 mm thick). Special samples with a square cross section (1.25 × 1.25 × 10.0 mm) were prepared to examine the field-induced strain behavior as the applied field direction changed (90°). Temporary electrodes were painted on ceramics with an acetone diluted sliver ink (Dupont 7095). The electrodes were dried

in a conventional oven at 80 °C for 25 min. After the field-induced strain in this direction was measured, the temporary electrodes were removed by acetone. The sample was then rotated 90°, and the temporary electrodes were reapplied. The samples were then ready for the field-induced strain measurement in the new direction. To minimize the dynamic effects from the nucleation and growth process, the driving field for the strain measurements was controlled to near a direct current (dc) condition (i.e., between 0.01 and 0.05 Hz).

III. RESULTS AND DISCUSSION

Figure 3 shows the change of spontaneous polarization and coercive field with respect to temperatures from 25 to 105 °C. These data were determined by a modified Sawyer–Tower circuit as a function of temperature (at 0.05 Hz). The results indicate that both the spontaneous polarization and the coercive field increase almost linearly as temperature decreases. A similar behavior has also been found for barium titanate at different phase regions.[9] The slight deviation from the linear relationship between 90 and 83 °C can be attributed to the development of a short-range interaction in the lattice when material transforms from a high temperature to a low temperature rhombohedral structure.[10] Because the spontaneous strain developed upon phase transformation (PE-to-FE) varies quadratically proportional to the dielectric dipole in the polarization direction,[11] it is conceivable that as the temperature decreases and the structure anisotropy increases it will make the nucleation and growth process in the field direction more difficult. As a result, the coercive field increases under the same driving condition and the rate of nucleation and growth of new domains[5] decreases. The data also indicate that at higher temperatures, where the spontaneous polarization and coercive field are small, the material can be more easily poled to saturation. With these benefits, it is a common
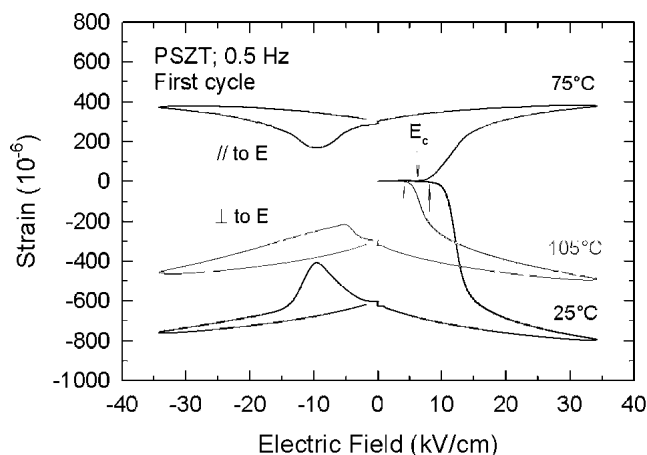
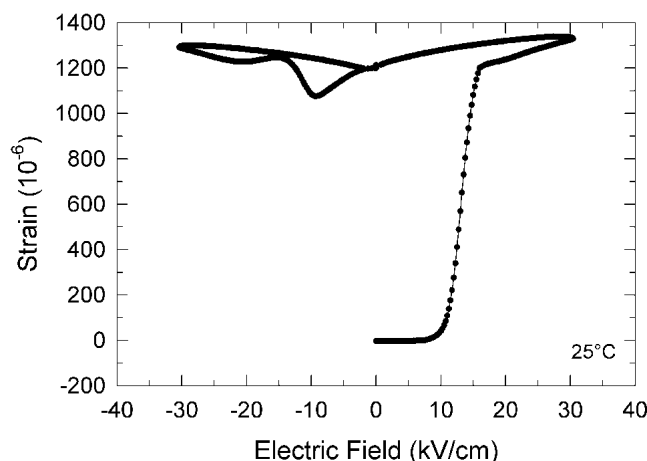FIG. 1. First field-induced strain behavior for the PSZT ceramics at different temperatures.

FIG. 2. The electrically induced strain in the field direction for ceramics with a thin cross section (0.25 mm thick)
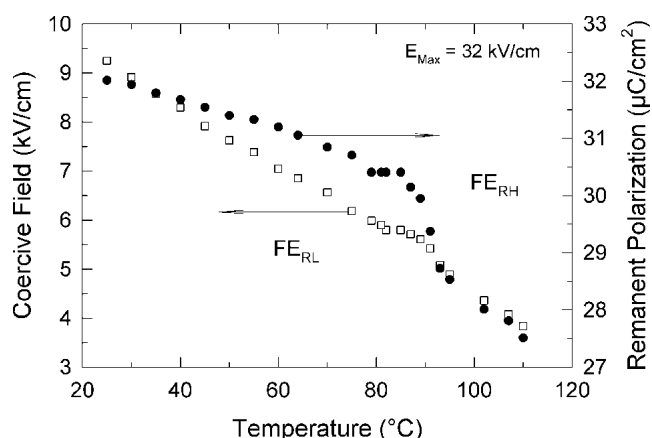
FIG. 3. Temperature dependence of the spontaneous polarization and the coercive field for the PSZT ceramics.

practice to electrically pole the ferroelectric materials at a temperature close to the Curie point (commonly referred as a "hot pole" process).

Figure 4 illustrates the electrically induced longitudinal strain hysteresis at room temperature for a square cross-section sample. The spontaneous strain is large in comparison to those at elevated temperatures. The space group of the PSZT ceramics for this composition at room temperature is confirmed to be $R3c$, which is the low-temperature rhombohedral phase. Upon the first application of an electric field in the Z direction (0°, 1st cycle, shown by the closed dark circles with line), the induced strain parallel to the poling direction increases rapidly during the first quarter cycle until reaching a maximum at the maximum field strength. Upon releasing the electric field to the zero and moving toward the negative direction, the induced strain shows a linear response, which corresponds to a converse piezoelectric effect. When the applied field in the negative direction is greater than the coercive field, the field-induced strain increases slightly toward saturation. The process repeats as the electric field reverses. The magnitude of field-induced strain during the first quarter cycle is 0.125% and during subsequent cycles is 0.01%. The dramatic difference in the field-induced responses between the first quarter cycle and subsequent cycles suggests that there are different mechanisms involved in these polarization reversal processes. As the external field is removed, a permanent deformation sets in (a remanent strain). When the electronic signal created by the permanent strain is compensated and the field-induced strain is re-measured again, the strain hysteresis (0°, 2nd cycle, with closed dark circles and line) shows the same behavior without the initial large increase in the field induced strain, indicating that after the first quarter cycle the initial mechanism involved with the field-induced stain from the virgin sample has disappeared. However, when the sample is

rotated 90° (90°, 1st cycle, shown by the open circles without line), a large field-induced strain during the first quarter cycle appears again followed by a small magnitude of strain hysteresis under the alternating current (ac) field driving condition. A similar field-induced behavior for the subsequent cycles is observed by following the same procedure after the electronic signal created by the remanent strain is electrically compensated (90°, 2nd cycle, with open circles without line).

Although the initial quarter cycle of the strain measured after the sample was rotated is slightly less than that from the virgin loop, the reappearance of the large initial field-induced strain is intriguing. The observation suggests that during the initial quarter cycle strain measured in the virgin material and right after 90° rotation is different for the subsequent field cycling. Based on a pseudo-cubic perovskite structure, the possible polarization rotation directions for this crystal structure are either 71° (or 109°) or 180°. Of these options, only 180° polarization reversal provides no changes in the magnitude of field-induced strain. Reorienting of a non-180° (71° or 109°) domain will give rise to a greater stain change. Therefore, it is plausible to assume the observed initial large strain of the first quarter field cycle is primarily associated with the reorientation of these non-180° domains, and in the remaining cycles most dipoles are switching by a 180° reversal. Because the spontaneous polarization directions in the virgin material are completely random and because most dipoles in the rotated sample are aligned almost perpendicular to the electric field, the growth of new domains in the applied field direction involves a large macroscopic strain development due to reorienting of the non-180° domains. Once the majority of the dipoles are aligned to the field direction, the torque experienced on the dielectric dipoles in the material during the next polarization reversal process is greatly reduced. As a result, the reorientation of the non-180° domains will become less favorable. The above interpretation, based on these electromechanical measurements, requires closer scrutiny. Especially since this is contrary to the general belief that the strain associated with domain switching is primarily due to a non-180° domain reorientation process. To reconcile this discrepancy, we compared the differences in the texture development of a poling process and a pole/depole process with the as-sintered sample. A poling process is a quarter cycle field driving process where a dc field is applied and released. A pole/depole process can be described as a half cycle driving condition,[4] where the randomly distributed dipoles in the virgin material are first poled to the field direction followed by a carefully controlled reverse field until the polarization decreases to zero where the external field is removed. During this process, it is expected that half of the domain configuration will be changed as the macroscopic polarization
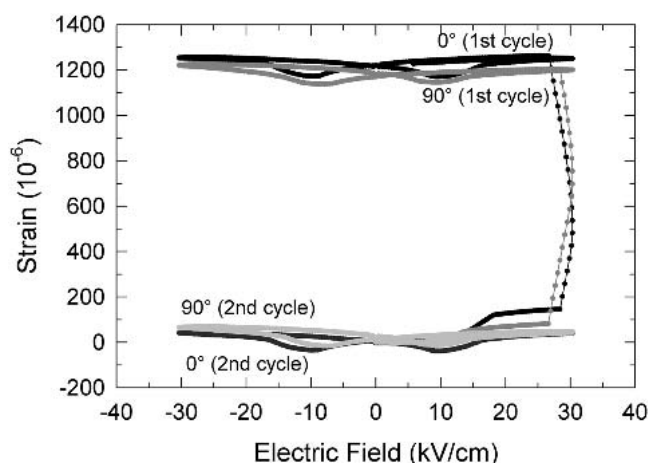

FIG. 4. Field-induced strain for PSZT ceramics with a square cross-section (1.25 × 1.25 mm) at room temperature.

decreases from the remanent value to zero. If the pole/depole process is dominated by domain reorientation changes other than 180° switching, the diffraction intensity in the pole/depoled sample will change with respect to the poled sample and show a stronger resemblance to the as-sintered sample. Figure 5 shows the x-ray diffraction intensities for these samples. The indexation of these diffraction peaks is based on a rhombohedral unit cell with space group $R3c$. Comparing the relative intensity change for the (222) and (200) peaks between the as-sintered and poled sample, it is found that after poling the relative intensity of (222) increases, which is in accordance with the increase of the macroscopic polarization in the field direction. The additional shoulders observed near these peaks in the diffraction pattern, with half of the total diffraction intensity, are the result of copper $K_{\alpha 2}$ radiation from the x-ray source. For the sample that was poled/depoled, the relative intensity between the (222) and the (200) peaks is similar to that of the poled sample, indicating that during the polarization reversal process, the dipoles in the dielectric material have not been randomized as the net remanent polarization has been canceled. The relative intensity remains similar between poled and poled/depoled samples, which strongly indicates that the 180° dipole reorientation is the dominant mechanism during the polarization reversal under an ac field condition in these rhombohodral PSZT ceramics.
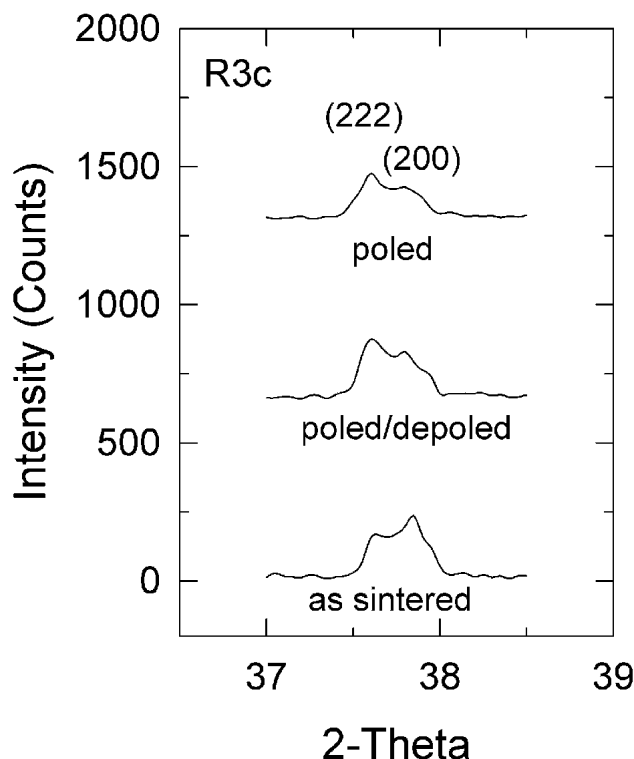
It is believed that the relatively small field-induced strain change after the first quarter cycle under an ac condition is due to the reorientation of some small highly strained domains where only the 71° domain reorientation process can be operated. The creation of these small yet highly strained domains could be the result of self-adjusting processes to minimize the total stored elastic energy and depolarization field in the ceramic during the poling process. Based on the differences in the magnitude of field-induced strains, there are less than 8% of these highly strained domains left in the ceramic during the poling process. This estimation seems to be slightly greater than Little's observation[7] where some residual domains (less than 5%) with different polarization direction will be difficult to completely remove in single crystal barium titanate under a high reverse field. With a polycrystalline microstructure, grain boundaries could play an important role in balancing the domain configuration[12,13] and the elastic energy created by the poling process. Therefore, the elastic clamping due to the grain boundary confinement might enhance the total amount of these highly strained domains in the ferroelectric ceramics.

Figure 2 illustrates the field-induced longitudinal strain for a virgin sample with a thin cross section (0.25 mm thick) at room temperature. The corresponding field-induced transverse strain is shown in Fig 1. In comparison with the field-induced strain in Fig. 4, the abrupt strain development in the field direction near 30 kV/cm for the square-cross section sample is quite unusual. While we have no explanation for this behavior at the present time, it is believed that the difference might be attributed to the sample geometry where samples with a thin cross section and a square cross-section experience a plane stress condition and a plane strain condition, respectively.[14] Data, once again, confirm that there is a magnitude difference in the field-induced strains between first cycle and subsequent loading conditions. More importantly, this observation demonstrates the importance of sample geometry on the field-induced deformation behavior.

It is worth noting a similar strain behavior reported for the electric field-assisted antiferroelectric-to-ferroelectric phase transformation[15] where a large transformational strain is first induced then followed by a small strain hysteresis during subsequent domain reorientation process. The major difference is the field-induced strain behavior reported in this paper does not involve a transformational strain as the field-assisted phase transformation reported by Yang and Payne.[13] This argument manifests itself when the observed field-induced transverse strain is negative during the poling process due to the dipole alignment (Fig. 1 the field induced strain behavior for 25 and 105 °C), while the field-induced transformational strain is positive in both parallel and perpendicular directions[16] due to the change of unit cell volume and crystal symmetry.

FIG. 5. X-ray diffraction patterns showing the texture development of poled, poled/depoled, and as-sintered samples.

IV. CONCLUSION

The differences in polarization processes during the initial poling process and subsequent cycling for the rhombohedral ferroelectric ceramics (PSZT) has been studied. The electromechanical responses for these domain processes are confirmed by the texture development determined by x-ray analysis. Experimental evidence indicates that the large initial field-induced strain in the first quarter cycle is dominated by the reorientation of the non-180° (or 71° and 109°) domains. During the subsequent cycle the majority of domains are reoriented by a 180° switching at the coercive field. As a result, the magnitude of field-induced strain is reduced significantly in comparison with the initial poling strain. A small strain hysteresis observed after initial poling can be attributed to the non-180° domain reorientation associated with small yet highly strained domains in the polycrystalline ceramics.

ACKNOWLEDGMENT

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